

A NEW METHOD FOR MEASURING HYPERGOL SCRUBBER EMISSIONS*

by

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ABSTRACT

Hypergolic propellants are used in spacecraft such as Space Shuttle, Titan, and others launched at Kennedy Space Center (KSC) and Cape Canaveral Air Force Station (CCAFS). Fueling and deservicing spacecraft constitute the bulk of operations in which environmental emissions occur. Monomethylhydrazine (MMH), nitrogen tetroxide (N_2O_4), and hydrazine (N_2H_4) are the main propellants of concern. Federal and State regulations require that KSC and CCAFS measure the amount of hypergols released to the environment. However, existing stack monitoring procedures are not applicable to hypergol operations that are intermittent and forced through the scrubber by inert gases, either nitrogen or helium.

NASA and I-NET Space Services developed and validated a method to measure the emissions of toxic vapors under conditions where measurement of the total flow rate through a scrubber is difficult if not impossible to determine. This method is based on: (1) accurate measurements of the scrubber efficiency (EFF) for each type of operation, (2) an estimate of the number of operations and their contributions to the total annual flow through the scrubber, and (3) a measure of the concentration change of toxic vapors trapped by or reacted with reagents in the scrubber liquor. The concentration change of the component of interest in the scrubber liquor before and after an operation can be used to calculate the emissions. For example, the increase of hypergol in the scrubber solution was used to calculate the amount of hypergol that passed through the scrubber:

$$\text{Emissions (wt.)} = [(1/\text{EFF}) - 1] \times \Delta (\text{wt. of hypergol})$$

Emissions based on the scrubber liquor compared closely with emissions measured under controlled conditions where gas concentrations and total flow rate were known.

A special sample system was constructed at the Toxic Vapor Detection Laboratory (TVDL) of KSC to measure hypergolic fuel or oxidizer in sample gas entering and exiting the test scrubber. The sample system was enclosed in a purged cart, except for tubing and valve electrical service leading to the sample ports and for sample valves positioned at the sample ports. This permitted operation of the sampling system during hazardous operations. This system and the data collected to validate the system are presented.

INTRODUCTION

This report describes a new hypergolic vapor scrubber monitor and a scheme for monitoring scrubber emissions without having to monitor gas flow and concentrations. The report includes data collected and analyzed in a proof-of-concept field test performed at Space Shuttle Launch Pad 39A fuel farm scrubber. The project scope includes field tests of all active hypergolic vapor scrubbers at KSC and CCAFS.

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A special sample system, made up of a sample cart and sample collection subsystems, was constructed at the TVDL to (1) collect MMH samples from gas entering or exiting fuel scrubbers or (2) collect nitrogen tetroxide samples from gas entering or exiting oxidizer scrubbers. The sampling cart consisted of pumps, valves, switches, and flow meters enclosed in a GN₂-purged cart. Sample-collection tubing, valve electrical service leading to the sample ports, and sample valves were positioned at the scrubber sample ports. All of this equipment was designed for use in a hazardous environment. The sample system was tested prior to the field tests in the TVDL with MMH and N₂O₄ vapor samples.

Lockheed Space Operations Company (LSOC) personnel connected sample lines to the Space Shuttle Launch Pad 39A fuel farm scrubber. Control samples were measured for a number of operating conditions without fuel flow. On the basis of these results, the scrubber sample ports were rinsed prior to the scrubber tests because controls indicated the sample ports were contaminated with MMH. LSOC Orbital Maneuvering System/Reaction Control System and I-NET TVDL/Contamination Monitoring Laboratory personnel in self-contained atmospheric protective ensemble (SCAPE) performed tests while other personnel from those organizations controlled the tests from the Launch Control Center. The operations were for a proof-of-concept test; hence, it was necessary to inject fuel vapor into the scrubber.

INSTRUMENTATION

Figure 1 is a schematic of the sample cart and sample collection tubes leading to the sample ports on the fuel scrubber. Also, the connections to the MMH storage tank are shown with the rotometer and flow line used to inject fuel into the scrubber. The fuel farm scrubber consists of two 2.5-foot-diameter, 6-foot-high towers, each packed with 3.5 feet of Tri-Pac 2-inch polypropylene spheres made by Tri-Mer Corp. Fuel-laden GN₂ flows upward in series through the two towers. The liquor, 150 gallons of 14-percent citric acid in water, is stored in a tank at the fuel farm. The liquor is pumped from the tank to the two towers, sprayed downward onto the packing in parallel 50-gallon-per-minute (gpm) streams, and then drained back to the tank. The liquor is reused until it reaches a specified percent of MMH, at which point it is replaced by fresh liquor.

Details of the sample cart and vapor scrub lines are shown in Figure 2. Half-liter bottles clamped on the cart exterior each contained 0.1 molar (M) sulfuric acid solution, which was pumped by tubing pumps to tees at the scrubber sample ports. Scrubber sample gas was also drawn into these tees by vacuum pumps in the purged cart. Liquid from the tubing pumps mixed with the sample gas at the tees, and the two-phase mixture was drawn into the bottles through 40 feet of 1/8-inch ID tubing, thus serving as a gas absorber in route to the half-liter bottles. This solution was circulated through the sample tubes to the tees and back during the sample period, which was sufficient to collect 1 liter (L) of inlet gas or 10 L of outlet or stack gas, i. e., several minutes.

The main scrubber flow was GN₂ coming through an aspirator, which had a nominal rate of 200 standard cubic feet per minute (SCFM) GN₂ (no outside air was allowed to enter). The fuel was injected by bubbling 10 SCFM or 20 SCFM of GN₂ through the MMH storage tank. The GN₂ entered the fuel storage tank from a valve-purge line at the bottom of the tank. GN₂, nearly saturated with MMH vapor (72- to 76-percent saturation), then flowed in succession through a storage tank vent pipe, into the liquid separator where it mixed with the aspirator flow, and finally into the scrubber. Three separate sample lines were installed, one each at the scrubber inlet, scrubber outlet, and stack outlet.

PROCEDURE

The test procedure is as follows:

1. Scrubber Preliminaries: Record the scrubber liquor volume in the tank reservoir before the scrubber pump is turned on. Take the scrubber liquor sample from the liquor storage tank while the scrubber pump is on, drain about 400 cubic centimeters (cc) into the waste bottle first, and then take a 400-cc sample into a clean bottle.
2. Cart Preliminaries: Flush the gas-sample fittings with water to remove any prior fuel contamination. Drain the gas sample tubes into the waste bottle. Place the fresh sample bottles containing the acid solution in the cart's bottle receptacles.

3. First 2-hour period: Start the aspirator flow through the scrubber (200 SCFM). Start the purge gas through the fuel tank at the desired flow rate (10 SCFM). Start the acid solution flow to sample ports in pairs, either the inlet and outlet or the inlet and stack.
 - When the acid returns to the bottle reservoir, thus flowing in a loop, switch the sample valve to draw the scrubber or stack samples. Note the initial volume of wet test meter.
 - Sample the inlet for 1 liter of gas and sample one of two outlets for 10 liters of gas.
 - At the end of the sample volume, switch the sample valve to ambient air suction and record the volume. Reverse the flow of the acid pump to drain all liquid back to the sample bottle. Remove and cap the sample bottle and check the bottle label.
 - Place the next pair of sample bottles on the cart receptacles and repeat steps 3 through 7 for the next planned sample locations.
 - After 2 hours (nominal), stop the above operations and take the scrubber liquor sample per step 1.
4. Second 2-hour period: Wait 2 hours (for SCAPE break), meanwhile maintaining the GN₂ flow at 10 SCFM. Then, take the scrubber liquor sample per step 1.
5. Third 2-hour period: At the start of this period, adjust the rotometer in the fuel tank purge to 20 SCFM. Repeat steps 3 through 8 for a nominal 2-hour period. Shut down operations.

RESULTS

Figure 3 shows the buildup of MMH in the scrubber liquor. The aspirator was on during the whole test, thus providing the main flow to the scrubber. An MMH tank purge of 10 SCFM for 198 minutes introduced 0.038-pound MMH/minute, for a total of 7.60 pounds. The switch to 20 SCFM tank purge for 95 minutes yielded 0.073-pound MMH/minute, for a total of 6.91 pounds.

Figure 4 shows the scrubber inlet, outlet, and vent stack MMH concentrations versus time. Efficiencies are noted on top of each bar. The time scale is approximate since gas samples were taken at irregular periods. The averages of these values were: inlet 1,171 ppm, outlet 2.67 ppm, and 99.772 percent efficiency; inlet 1,171 ppm, stack 2.06 ppm, and 99.824 percent efficiency.

Figure 5 shows inlet, outlet, and stack MMH concentrations were elevated when the MMH tank purge was doubled to 20 SCFM. The averages of these values were: inlet 1,905 ppm, outlet 4.86 ppm, and 99.745 percent efficiency; inlet 1,905 ppm, stack 4.42 ppm, and 99.768 percent efficiency.

The key concept demonstrated is that scrubber emissions can be calculated by a one-time measurement of scrubber efficiency and then by periodically measuring the buildup of fuel or oxidizer in the scrubber liquor reservoir. The equation for this calculation is:

$$\text{Emissions (wt.)} = [(1/\text{EFF}) - 1] \times \Delta (\text{wt. of hypergol}) \quad (1)$$

where the *emissions* is the calculated amount of fuel or oxidizer released during the period between the scrubber liquor samples and the *EFF* is a weighted average of typical operations.

Data from a proof-of-concept test are used to calculate the emissions two ways. First, flows and outlet concentrations are measured over a representative range of operational conditions. Such a test conforms to the standard EPA protocol for measuring stack emissions. Using these data, the emission value is simply the flow rate times the outlet concentration:

$$\text{EPA Emissions (wt.)} = \text{Flow Rate} \times \text{Outlet Conc.} \quad (2)$$

The *EFF* requires an inlet measurement:

$$EFF = (\text{Outlet Conc.} - \text{Inlet Conc.}) / \text{Inlet Conc.} \quad (3)$$

The second or *new* emissions method requires both a knowledge of *EFF* and samples of scrubber liquor to determine fuel buildup in the liquor. Equation 1 is then used to calculate the second emission value, and this is compared with the EPA method using equation 2 for a given time period. The comparison provides a basis for validation of the new emissions method.

Table 1 shows the emissions calculated from the tests reported here using equation 2. These emissions are to be compared with Table 2, which shows the emissions calculated from the same test using equations 1 and 3.

Table 1. Emissions Based on Standard EPA Method for Low and High GN₂ Purge Flow

Conditions	Flow Rate L/min	MMH Rate gm/min	Total MMH Emitted, gm
Low purge flow rate	7075	-----	-----
MMH flow rate at outlet	0.019	0.039	-----
MMH flow rate at stack	0.015	0.030	-----
Emissions at outlet	-----	-----	7.6
Emissions at stack	-----	-----	5.9
High purge flow rate	7358	-----	-----
MMH flow rate at outlet	0.036	0.073	-----
MMH flow rate at stack	-----	0.066	-----
Emissions at outlet	-----	-----	7.0
Emissions at stack	-----	-----	6.3

Table 2. Emissions Based on New Method for Low and High GN₂ Purge Flow

Conditions	gm
Low purge flow emissions	-----
Based on efficiency at outlet	7.9
Based on efficiency at stack	6.1
High purge flow emissions	-----
Based on efficiency at outlet	8.0
Based on efficiency at stack	7.3

So far the evidence is the concept was verified within experimental error. To highlight the data which lead to this conclusion:

1. The curve in Figure 3 shows a reasonably consistent buildup of MMH in the scrubber liquor reservoir during the test periods of low and high MMH tank purge, 10 and 20 SCFM. Note the buildup roughly doubled when the purge gas doubled, as expected.
2. TVDL gas concentration assays show a credible percent saturation for GN₂ exiting the fuel storage tank, 72 to 76 percent MMH.
3. The efficiencies and gas concentrations shown in Figures 4 and 5 for fuel scrubbers are in the range of earlier studies at KSC.

4. The emissions as measured by gas samples and gas flow rate, Table 1 (the standard EPA method), agree reasonably well with the emissions calculated by equation 1 using scrubber liquor sample assays. These data are summarized in Table 3. The agreement between the standard EPA and the new method is quite good considering the diverse paths in obtaining these results. There are experimental errors in each method. For example, scrubber gas and liquor ports could become contaminated if not flushed properly between each sample. Also, the primary gas flow value was based on standard orifice tables and was not verified by field measurement.

Table 3. Summary of MMH Emissions Measurements

Conditions	Standard EPA Method	New Method
	gm	gm
Outlet, low GN2 purge	7.6	7.9
Outlet, high GN2 purge	7.0	8.0
Stack, low GN2 purge	5.9	6.1
Stack, high GN2 purge	6.3	7.3
Total, outlet GN2 purge	14.6	15.9
Total, stack GN2 purge	12.2	13.4

CONCLUSIONS

The new method demonstrated in this project appears to be valid for fuel emissions based on the data in Table 3. That is, emissions based on the EPA method and those based on scrubber liquor buildup agree within experimental error.

Comparisons of outlet gas versus stack concentrations indicate an average lower amount of fuel in the stack outlet gas versus the scrubber outlet gas. However, the data were scattered enough such that the differences in outlet versus stack concentrations were not significant.

The scrubber efficiency did not vary significantly over the range of flows and concentrations in this test, i.e., 210 to 220 SCFM total flow. (However, it is desirable to extend the flow range to the lower values found in many typical purge operations; i.e., at 10 to 20 SCFM total flow.)

For these flow operations powered by an aspirator, the actual measured stack emissions are on the order of 3 grams of MMH per hour.

ACKNOWLEDGMENTS

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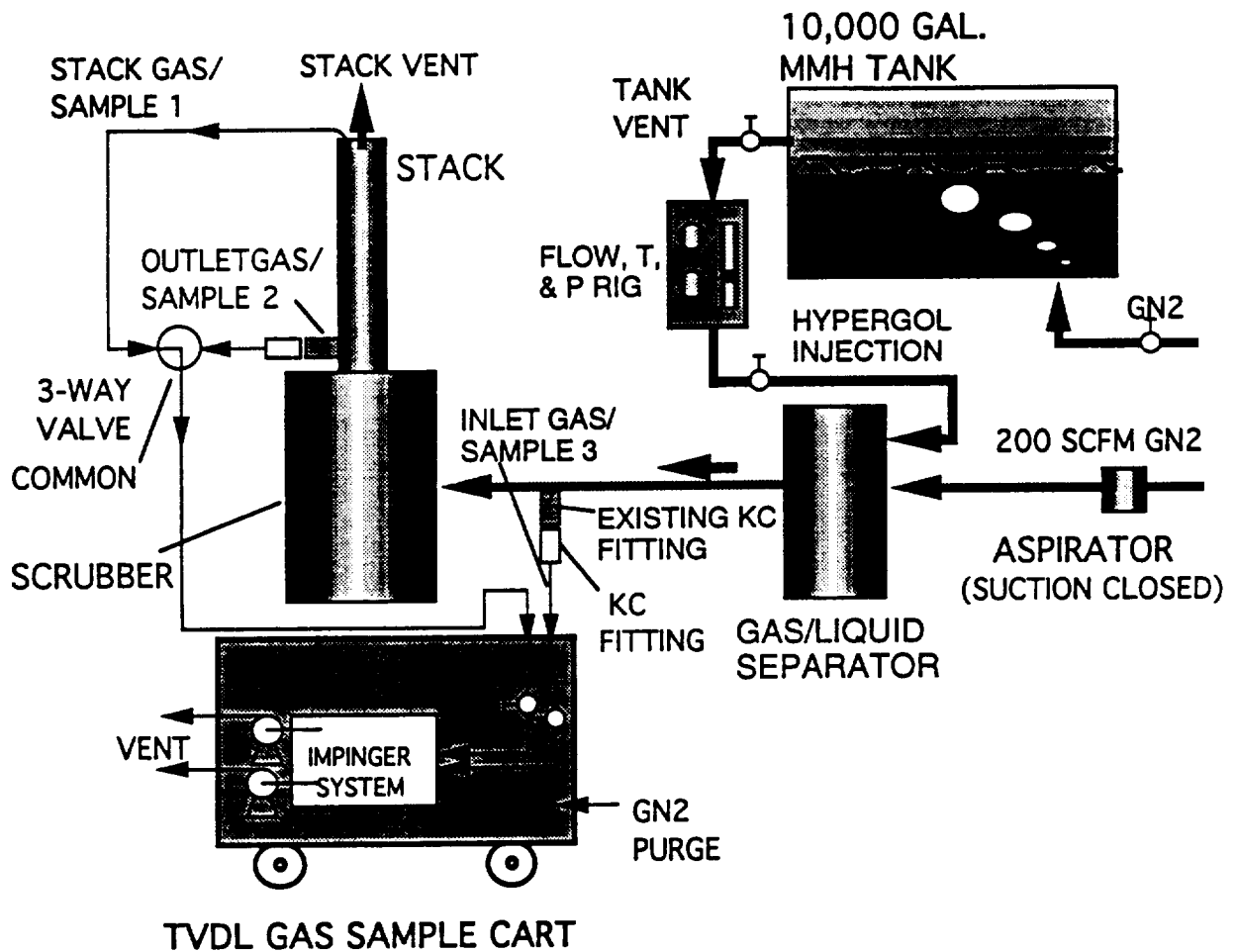


Figure 1. Field Test 1, hypergolic scrubber test setup on Launch Pad 39A, MMH fuel farm, 08DEC93

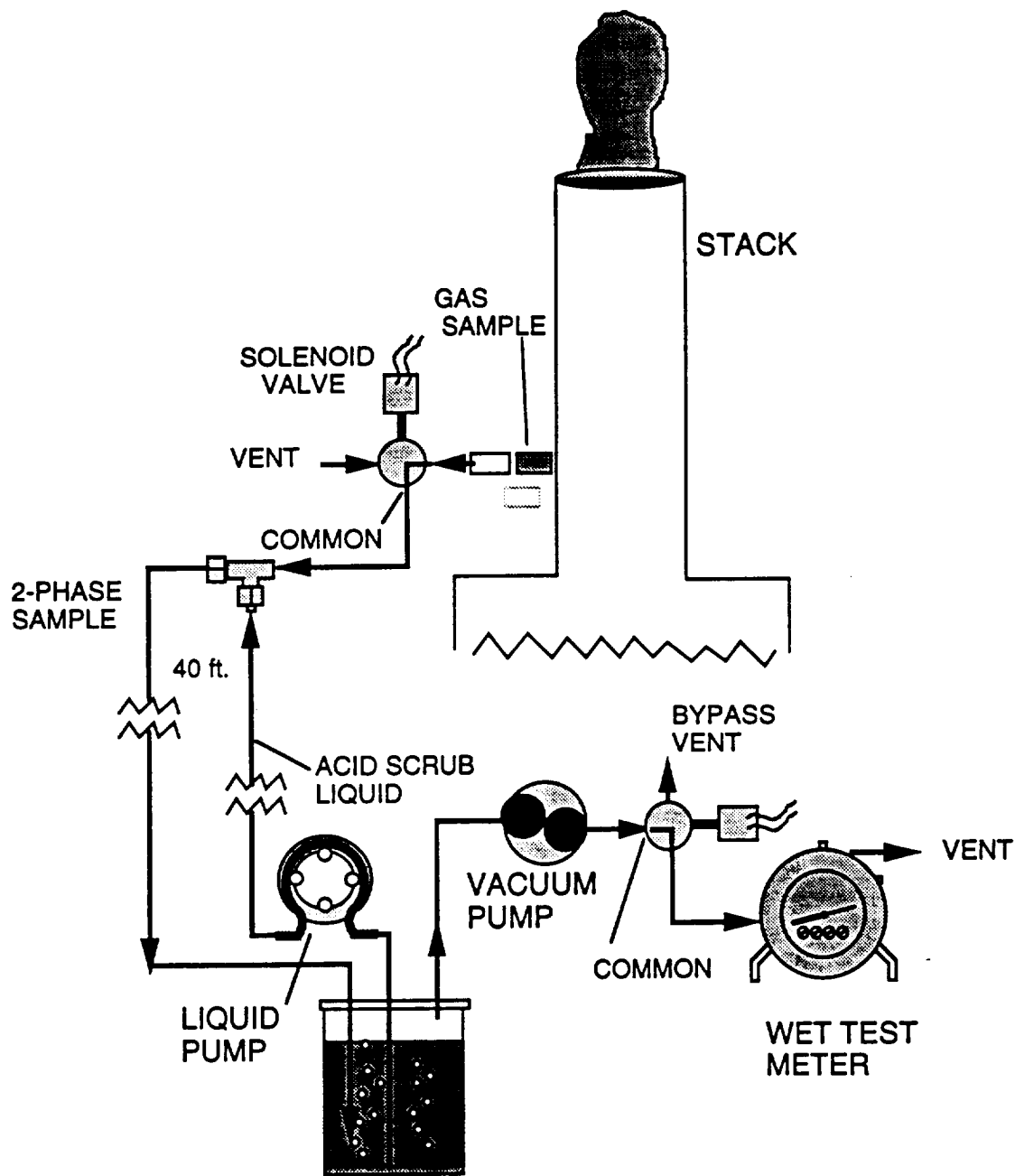


Figure 2. Details of acid scrub method for sampling MMH, Test 1
 (This sample loop was repeated three times as shown in Figure 1.)

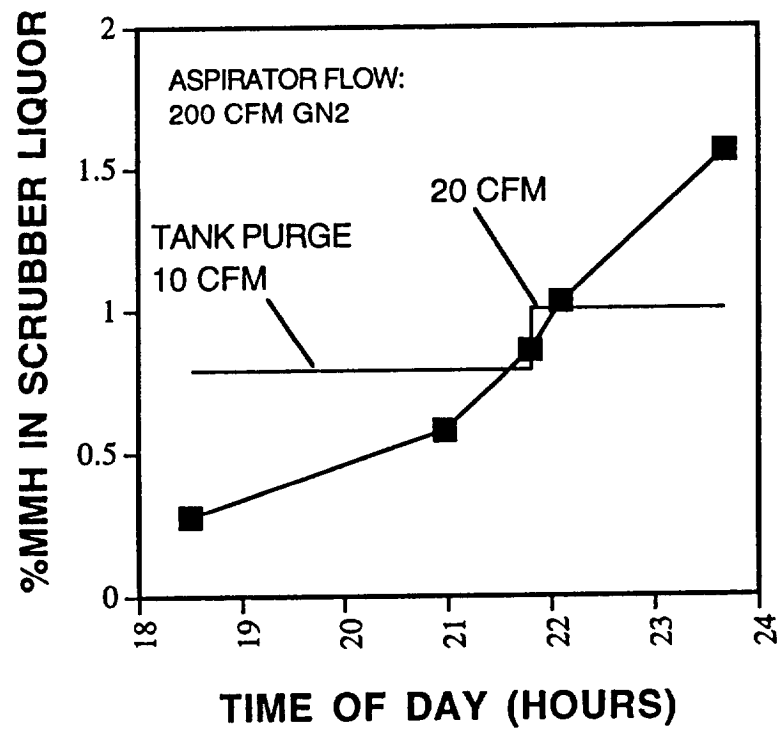


Fig. 3. Buildup of MMH in scrubber liquor reservoir

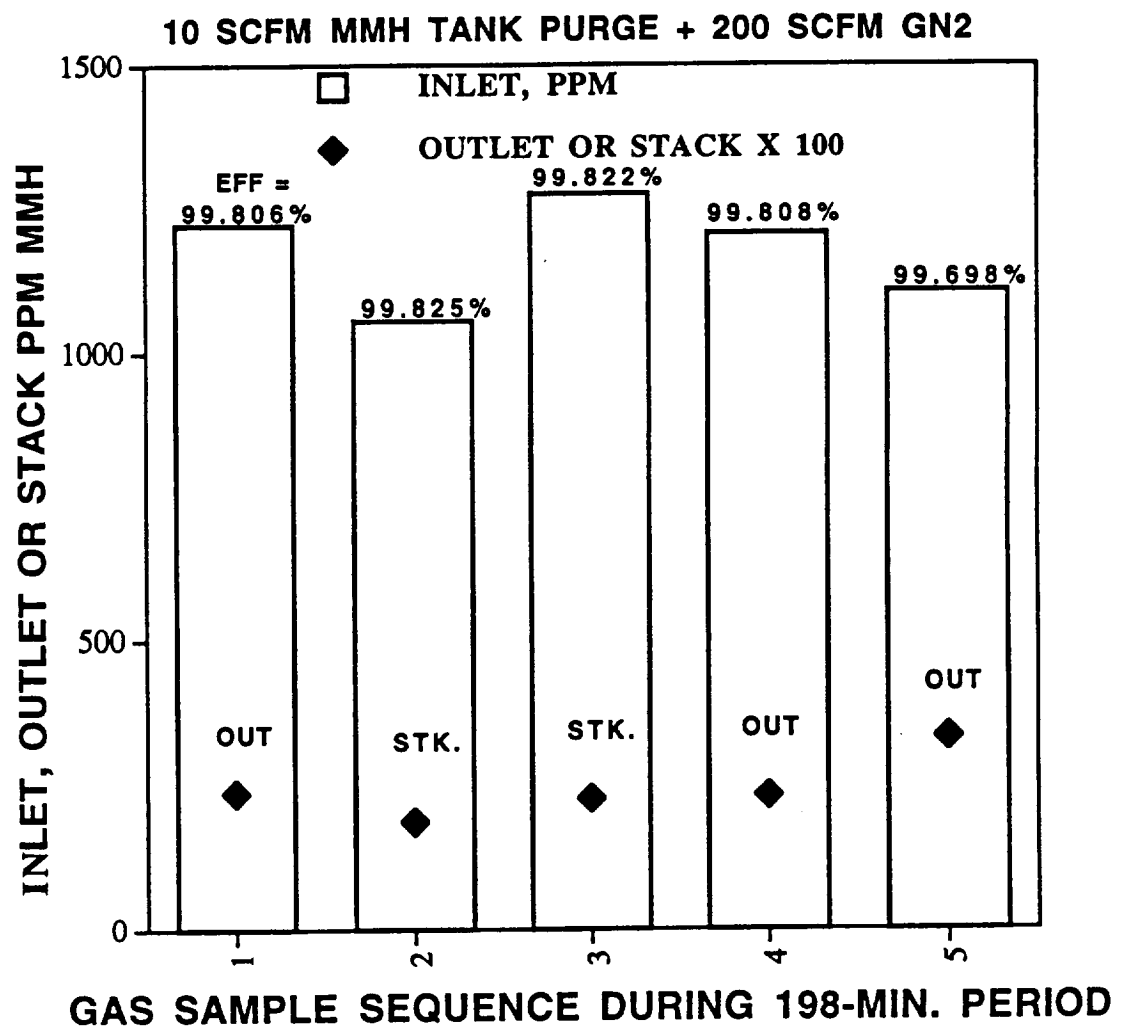


Fig. 4. MMH in gas samples and scrubber efficiency

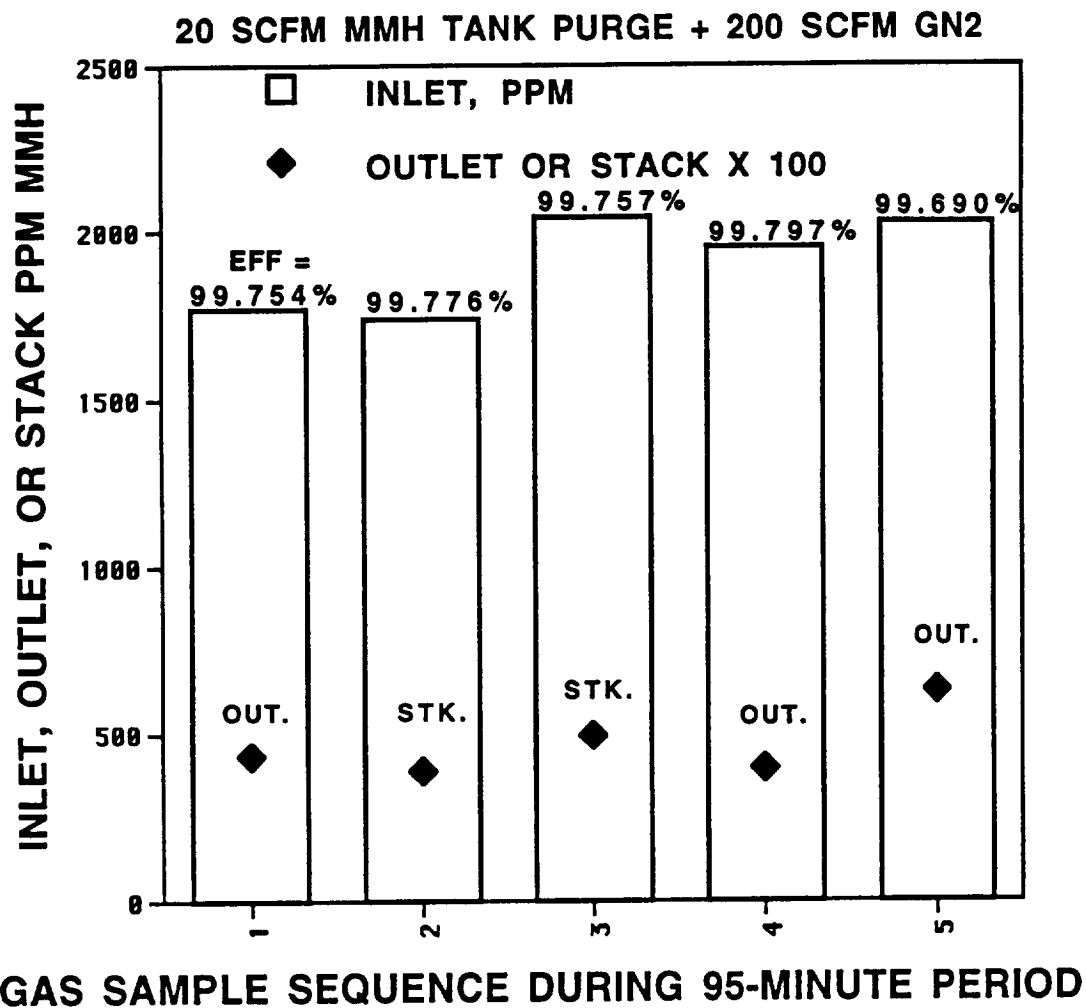


Figure 5. MMH in gas samples and scrubber percent efficiency